CONTAINERLESS PROCESSING OF MOLTEN TIN SAMPLES IN A CONTROLLED OXYGEN ENVIRONMENT

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[Abstract]

Contamination due to oxygen or oxide layer formation is a major concern in containerless processing of metallic melts. While experiments dealing with the studies of undercooling, nucleation, and observation of surface microstructures are influenced by even a surface monolayer, the problem is less acute for metals such as tin which have appreciable volubility for oxygen. The present study involves tin samples which were melted and resolidified inside a high temperature acoustic levitation chamber in a controlled low-oxygen environment. The processed samples were analyzed by sensitive surface analysis techniques (SEM/EDS anti XPS) to determine oxygen distribution on the outside surface and the cross-section. Results indicate that contamination due to oxygen can be avoided provided outgassing from all heated surfaces is minimized.

INTRODUCTION

Containerless experimentation with metallic melts requires a practically oxygen-free environment, Any significant residual levels of oxygen will result in a rapid metal oxide formation and alter the metallic transformations being studied. In experiments dealing with undercooling of metals, alloys anti metallic glasses, entry of oxygen into the melt can initiate premature nucleation and forestall the supercooling process. In addition, surface properties, such as surface tension and emissivity are likely to change drastically due to the build up of any surface oxide. The surface oxide will also interfere with the observation of surface microstructure.

The oxygen sorbents developed under the Microgravity Advanced Development Activities program at JPL can, in theory, lower oxygen to parts-per-trillion (ppt) levels provided there is minimal outgassing from connecting lines and other surfaces in contact with the cleaned gas. If oxygen levels can be maintained at or below ppt levels, sufficient time is generally available for experimentation before even an oxide monolayer is formed. Even if oxygen levels could not be lowered to ppt levels (either because of outgassing or due to inadequate gas cleaning), there are metals (e.g. tin anti copper) where even in the presence of a limited oxygen contamination, the metal oxide may riot appear as a separate phase due to the solubility[1] of the oxide in the melt.

The objective of the present work is to establish that metallic melts can be processed in microgravity containerless expcrin-rents without contamination by an external oxygen source, e.g. the sample environment. '1 he experiments involved the processing of high purity samples of tin in a high temperature acoustic levitator. 1 he tin samples were heated from room temperature to 300 °C, which is significantly above the melting point of tin of 232 °C. 'I he processed samples were analyzed for the presence of the oxide (or oxygen) on the outer surface as well as in the cross-section. Such an analysis is crucial to determining whether processing of metallic melts can be carried out without incorporating unacceptable levels of oxygen contamination.

EXPERIMENTAL

1 wo modes of gas purification were used. In the first mode, a commercial t lydrox purifier (Matheson Gas Co.) was used and the gas in the processing chamber was recirculated in a closed loop and cleaned by its passage through the purifier. In the second mode, high purity argon was passed through a bed of copper zeolite (activated by reduction) before entering the high temperature acoustic levitator. '[he scrubbed argon gas provided the low-oxygen environment around the sample and then exited the levitator chamber through an exit port. '1 he schematic for this mode of operation is shown in Figure 1. Details on the preparation of the activated oxygen sorbent bed and its oxygen uptake characteristics are given in References 2 and 3.

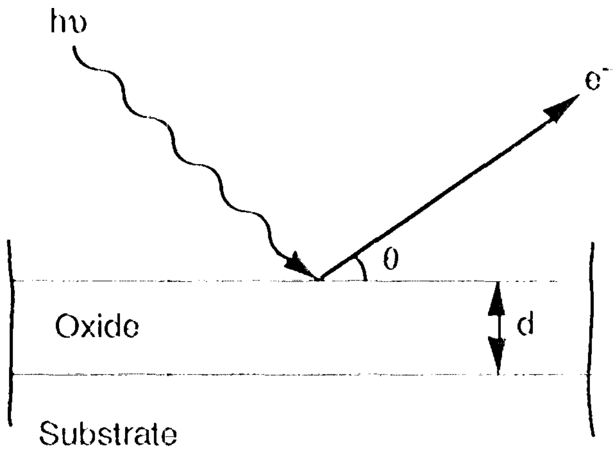
1 in metal samples were cut from a high purity (99.9999%) metal rod. 1 hey were transferred to the levitator by means of a teflon suction tube which lifted the sample pellet from a bottle and placed it on a zirconia plate through a port in the levitator chamber. After placing the metal sample on the zirconia plate inside the levitator chamber, the chamber porl was capped off and the system was pumped down to 10^{-7} torr. The chamber was then back filled with high purity argon at about 1 atm. Heating of the sample was then initiated by means of nichrome heaters inside the chamber. 1 he argon purity inside the chamber was maintained by operation in one of the two modes described above. 1 he total pressure inside the levitator was limited to just below 5 psig. 1 he sample temperature was taken to be the same as that of the zirconia plate and was measured with a thermocouple. When the sample temperature reached the target value of 300 °C, it was maintained at this value for 30 minutes. 1 hereafter, sample heating was terminated and the system was allowed to cool down. When the sample temperature was close to room temperature (below 50 °C) and the gas purification systems properly cooled down, the sample was removed and placed in a secure! glass bottle for subsequent analysis.

The analysis of the processed metal samples was carried out using Scanning Electron Microscopy with Energy Dispersive Spectrum (SEM/EDS) and by X-ray Photoelectron Spectroscopy (XPS). '1 he outer surface of all processed samples and a few "as received" samples was analyzed. In addition, the processed tin samples were cut to expose the cross section for similar surface analysis.

RESULTS AND DISCUSSION

Surface analysis on four different samples of "as received" (e.g. not contaminated by handling) tin was conducted by SEM/EDS and XPS. These samples were labeled Sn-3, Sri-6, Sri-7, and Sri-8.

Figure 2 shows the SEM/EDS scan obtained from the fresh sample Sri-3. This scan shows a main peak and some secondary peaks for Sn while only a very small peak for oxygen resulting from the surface oxide. In the XPS analysis on this sample, tin and oxygen peaks were clearly seen in the spectrum. Figure 3 shows the wide XPS scan for sample Sri-3 with tin and oxygen peaks while Figure 4 shows the Sn 3d peaks on an expanded scale of the binding energy for the same sample. Note in Figure 4 that the position of the taller peaks is for tin present as an oxide whereas the relatively smaller shoulder on the right is for tin present as a metal. The relative peak height of the taller peak (tin oxide) to the right shoulder peak (tin metal) leads to a rough estimate of the thickness of the oxide layer.



For an X-ray photon incident on a metal substrate with an oxide layer (see above diagram), the relative photoemission signal intensities (detected at angle θ) from the oxide and the metal may be expressed as:

$$\frac{I_{ox}}{I_{sub}} = \frac{D_{ox}\,\lambda_{ox}}{D_{sub}\,\lambda_{sub}} \cdot \frac{1-\exp(-d/\lambda_{ox}\sin\theta)}{\exp(-d/\lambda_{ox}\sin\theta)} \qquad (1)$$

where I is the signal intensity, D is the atomic number density, λ is the attenuation length of the photoelectrons, d is the oxide layer thickness, and the subscripts 'ox' and 'sub' refer to the oxide and the substrate, respectively. The relationship may be simplified by noting that the factor

$D_{ox}\,\lambda_{ox}\,/\,D_{sub}\,\lambda_{sub}$

is newly unity, and in the present measurements
0 = 350 and λ = ?0 Å.

By substituting these values in Equation (1), a simplified relationship is obtained between the ratio of the oxide! and the substrate signal intensities and the oxide layer thickness d.

1 bus, estimates of the oxide layer thickness of the "as received" samples from XI'S analyses were obtained and are shown in 1 able 1.

1 able 1. Estimates of the oxide layer thickness for "as received" tin samples as obtained from XI'S analysis.

SAMPLE ID	OXIDE LAYER THICKNESS, Å
Sn-3	29
Sri-6	23
Sri-7	**30**
Sri-8	26

1 he results in 1 able I indicate that the average oxide layer thickness on the fresh tin samples was 27 Å.

Samples Processed using the Hydrox Purifier

Samples Sri-l and Sri-2 were processed using the Hydrox purifier. At the end of melting and resolidifying, the samples were retrieved and analyzed by SEM/EDS anti XPS.

Surface analysis of the samples by SEM/EDS is shown in Figures 5 anti 6. It is seen that the oxygen peaks are more easily identifiable and are substantially larger than for the "as received" samples (cf. figure **2).** XPS analysis obtained on the processed samples Sri-l and Sri-2 are shown (on expanded binding energy scale) in Figures **7** and 8, respectively. 1 hese figures show that the shoulder' (representing tin as metal) on the right side of the main peak (tin as oxide) is now much smaller for both samples, 'Implying an increased oxide layer due to processing. 1 he estimated oxide layer thicknesses are 41 Å for Sri-l and 4? Å for Sri-?, as shown in Table II.

Samples Processed using Gas Scrubbed through the Zeolite Bed

The tin samples processed using purified argon gas obtained after scrubbing through the copper zeolite bed were labeled Sri-4 and Sri-5.

Surface analysis of the processed samples Sri-4 and Sri-5 by SEM/EDS is shown in Figures 9 and 10, respectively. It is seen from Figure 9 that practically no oxygen peak is detected whereas there is a small oxygen peak present in Figure 10. XPS analysis on samples Sri-4 and Sri-5 is shown in Figures 11 and 1?, respectively, which show the Sn 3d peaks on an expanded binding energy scale. It is seen from Figure 11 (sample Sri-4) that the right shoulder peak (corresponding to tin metal) is quite pronounced. However, from Figure 12 (sample Sri-5), the right shoulder peak is rather small. These results suggest that the oxide layer thickness is greater for sample Sri-5 than for sample Sri-4. Quantitative estimates of the oxide layer thickness may again be made using the ratio of the signal intensities corresponding to tin as oxide and tin as metal, respectively. The results obtained are 24 Å for Sri-4 and 37 Å for Sri-5 as shown in Table II. Due to the higher oxide layer thickness of sample Sri-5 compared to the average oxide layer thickness of fresh samples, it would appear that this sample picked up some contamination during processing. This probably resulted from inadequate outgassing of the levitator chamber parts during processing of this sample. Sample Sri-4, on the other hand, compares well with the fresh samples and shows no evidence of contamination.

Table II. Estimates of the oxide layer thickness for processed tin samples obtained from XPS analysis.

SAMPLE ID	SURFACE ANALYZED	OXIDE LAYER THICKNESS, Å
Sri-l	OUTER	41
Sri-?	OUTER	42
Sri-4	OUTER	24
Sn-5	OUTER	3-/
Sri-?	SECTION	24
Sri-4	SECTION	?1

Sample Cross-Section Analysis

Cross section analysis was conducted on samples Sri-? (processed with gas recirculation using Hydrox purifier) and Sri-4 (processed with gas scrubbed through the zeolite bed).

The metal samples were cut at the middle into two pieces using a sharp cutting edge. The freshly exposed surface from the interior of each sample was analyzed by SEM/EDS and XPS.

Figures 13 and 14 show the SEM/EDS scans obtained for the cross-sectional surfaces of Sri-? and Sri-4, respectively. Note that Figure 13 (sample Sri-?) shows only a very small signal peak for oxygen while Figure 14 (sample Sri-4) shows almost no oxygen. Figures 15 and 16 show the Sn 3d peaks in the XPS spectrum on an expanded binding energy scale. For both of these samples, it is seen that the shoulder peaks corresponding to tin (as metal) are significant. More quantitatively, an oxide layer thickness of 24 Å is obtained for the cross-section of Sri-? and 21 Å for the cross-section of Sri-4.

1 he above results suggest that a lower amount of oxygen is present on the cross section than on the surface for both samples, and the cross-section of Sri-4 has lower oxygen than the cross-section of Sri-?. '1 hese results are in agreement with the outer surface analyses for samples Sri-? and Sri-4 which indicate that the outer surface of sample Sri-4 gained no additional oxygen during the melt processing while sample Sri-2 had picked up some oxygen contamination.

Future work will involve melting and resolidifying metal samples inside an environmental control chamber at JPl . 1 he gas inside the chamber will be cleaned using the JPL -developed sorbents for removing oxygen and water vapor. 1 he metal samples will be melted using beam heating and other heating techniques being currently evaluated.

CONCLUSIONS

1 hese results indicate that tin samples can be processed (by subjecting them to the melting and resolidifying cycle) inside a positioner chamber in a sufficiently pure gas environment provided by scrubbing through a bed of copper zeolite. Such processing will not add oxygen to the sample beyond what is already deposited on the fresh sample. The results also indicate that if the heated components are not properly outgassed, oxygen contamination will result.

ACKNOWLEDGMENTS

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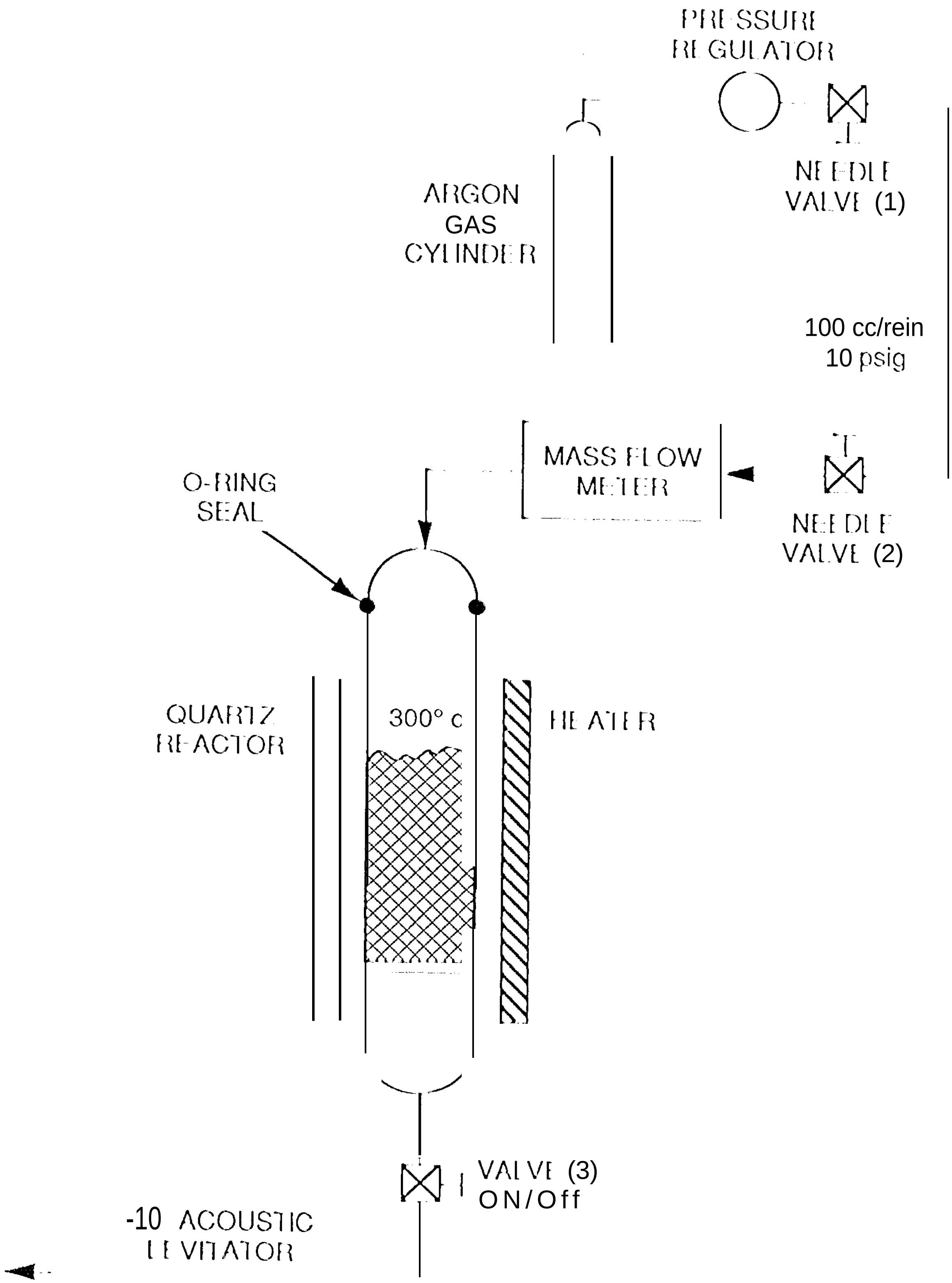

Figure 1. Schematic of Experimental Set Up for Supplying Oxygen-free Argon to the Acoustic Levitator

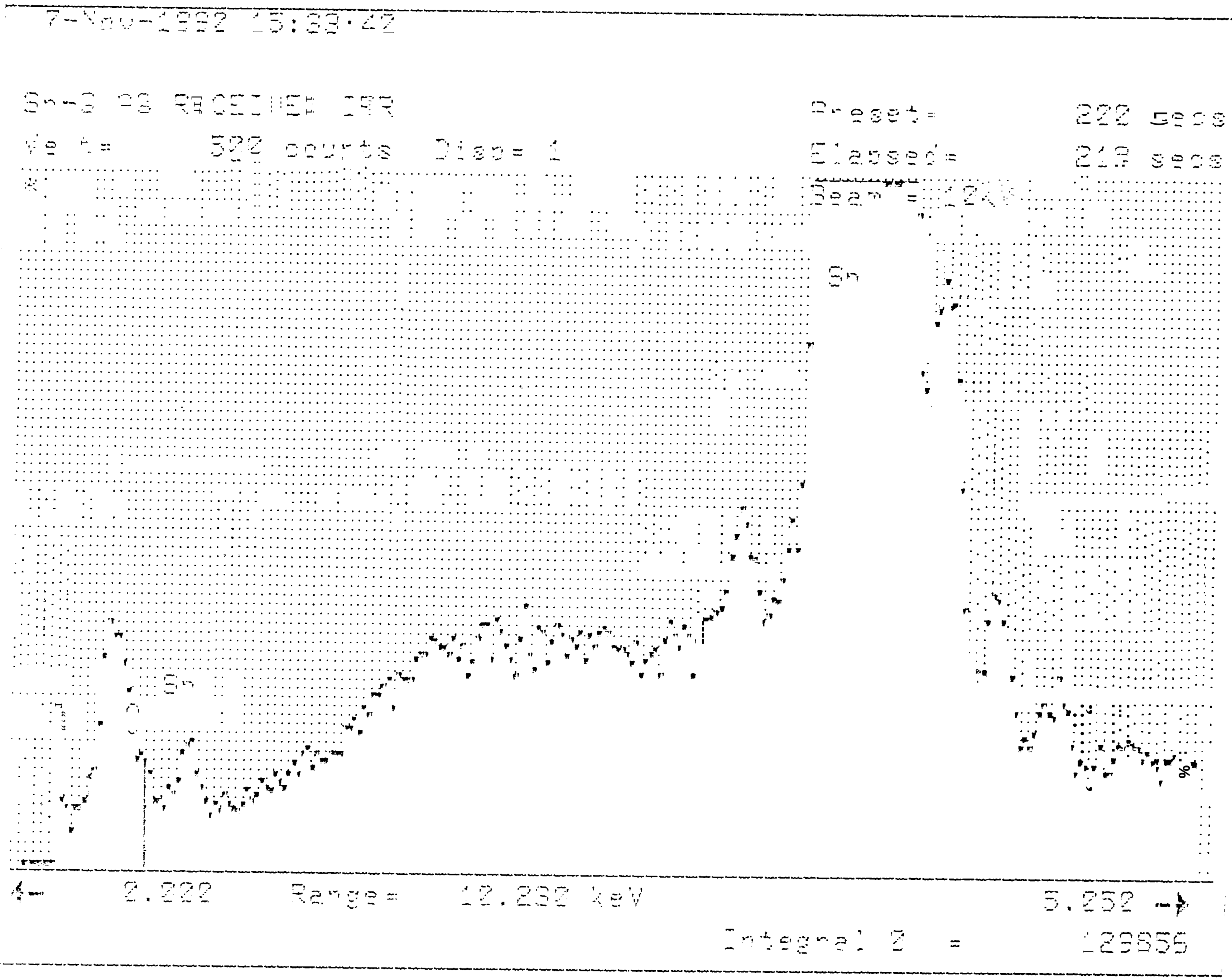

Figure 2.2 SEM/EDS Scan for Sample Sn-3

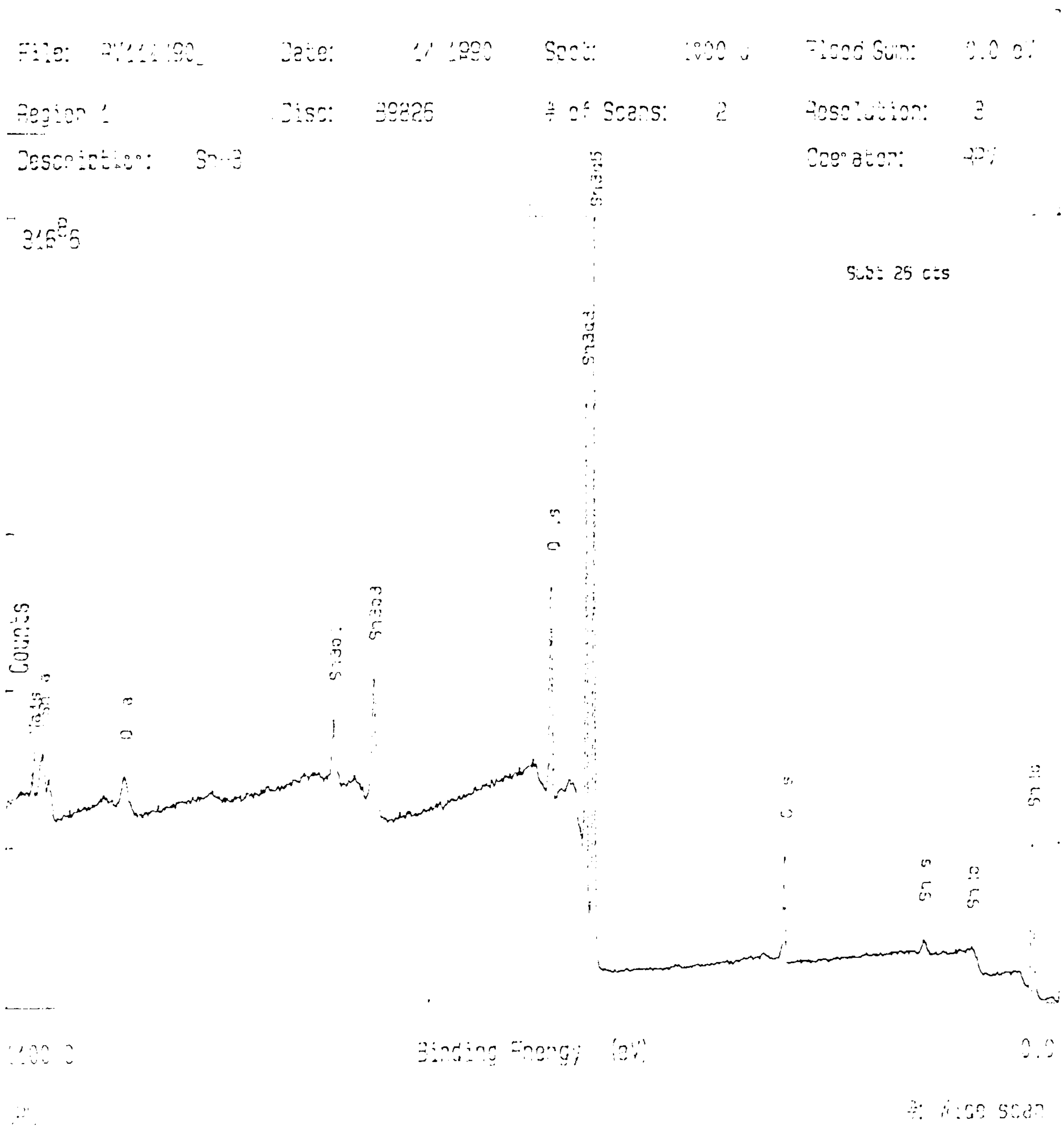

Figure 1.3 XPS Wide Scan for Sample Sn-3 Surface

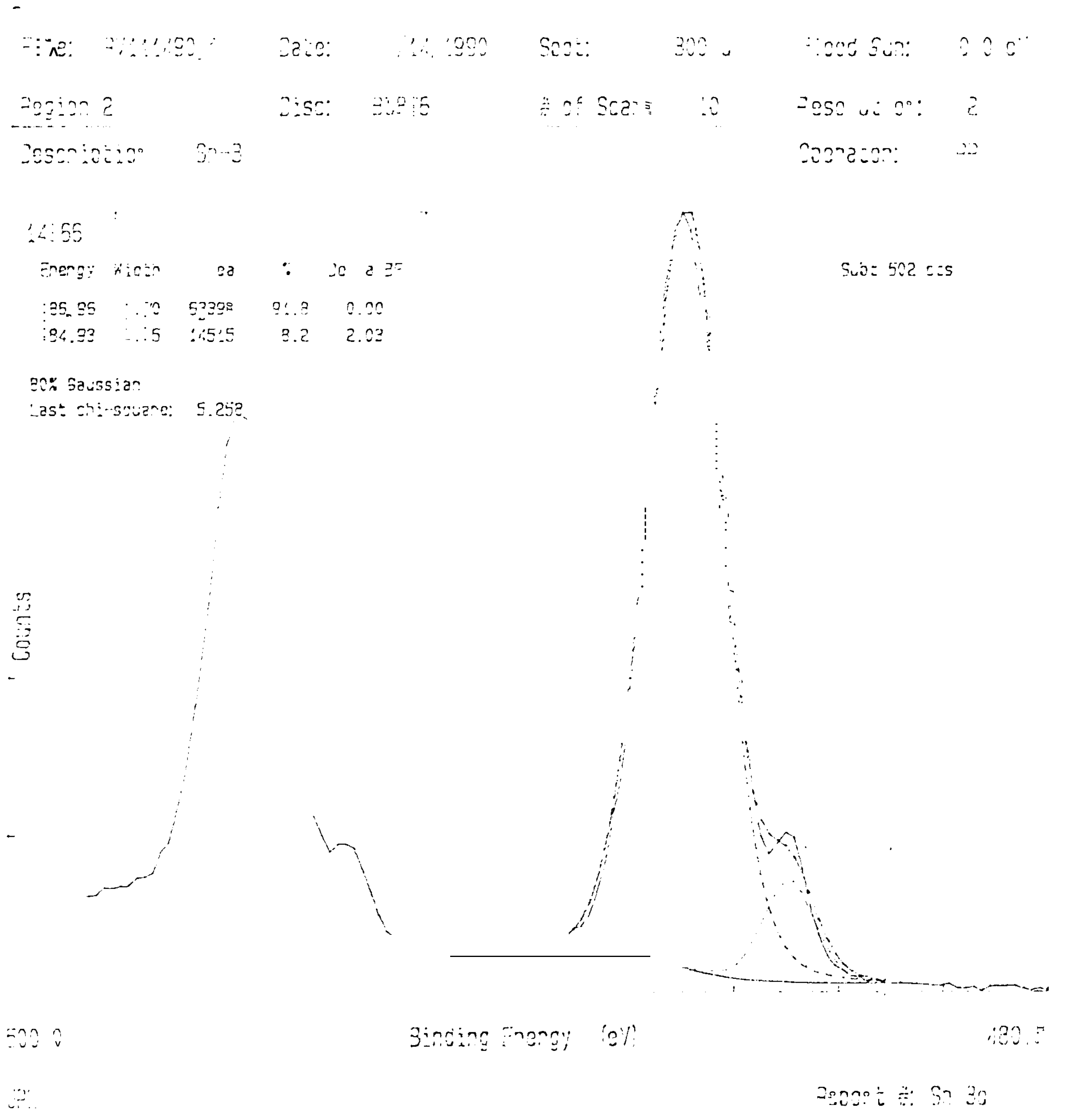

Figure 2.4 XPS Scan of Sn 3d Peaks for Sample Sn-3 Surface

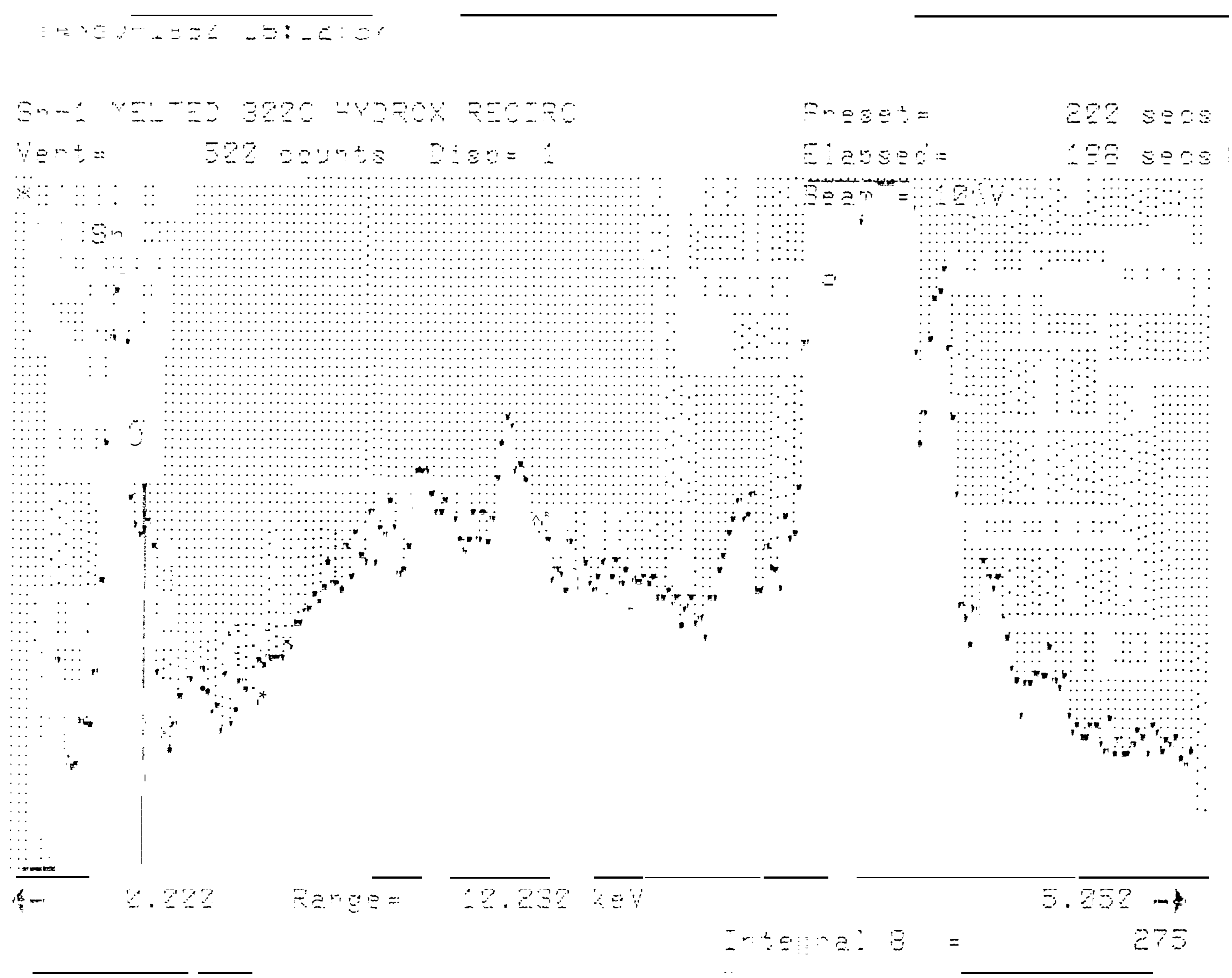

Figure 10.5 SEM/EDS Scan for Sample Sn-1 Surface

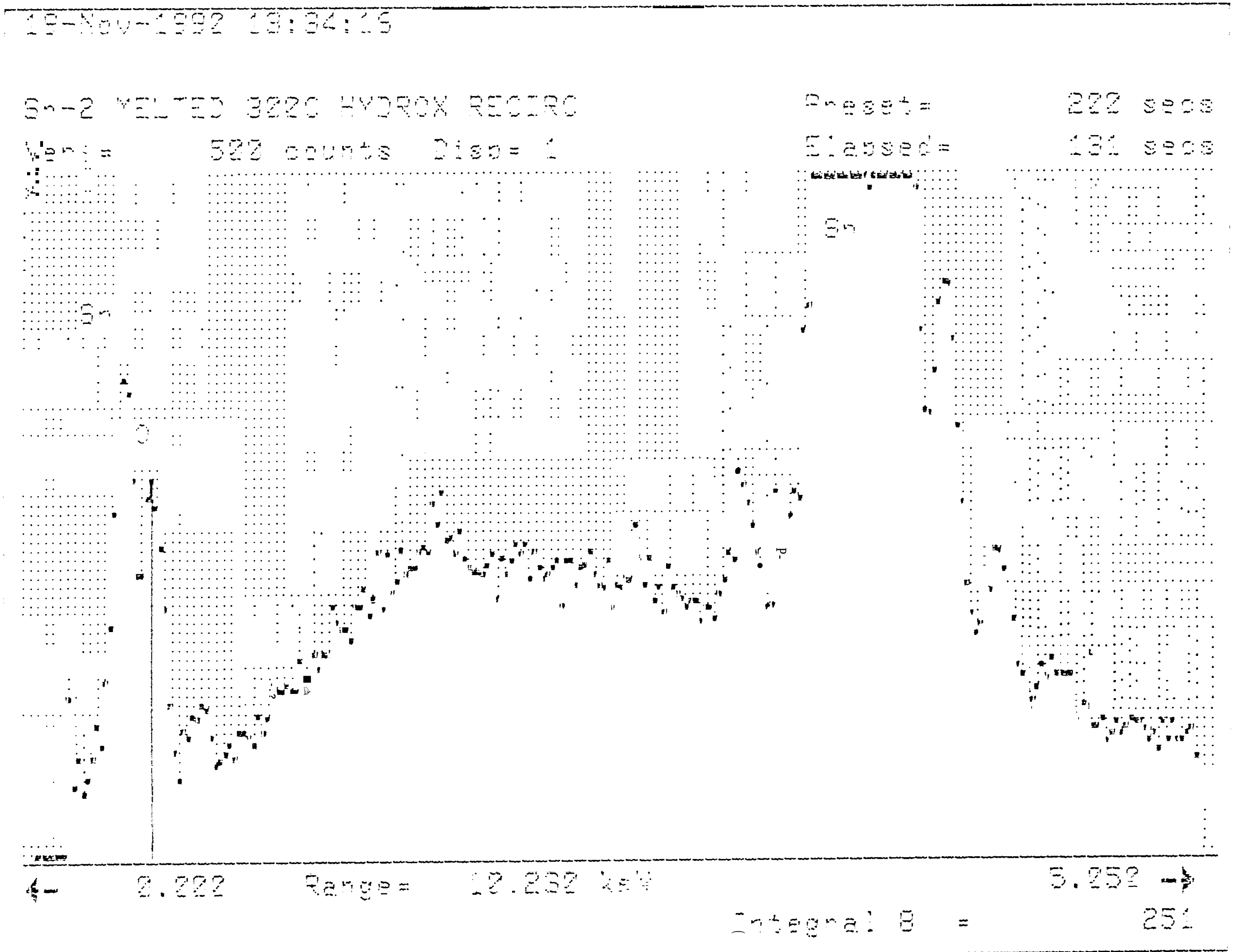

Figure 16. SEM/EDS Scan for Sample Sn-2 Surface

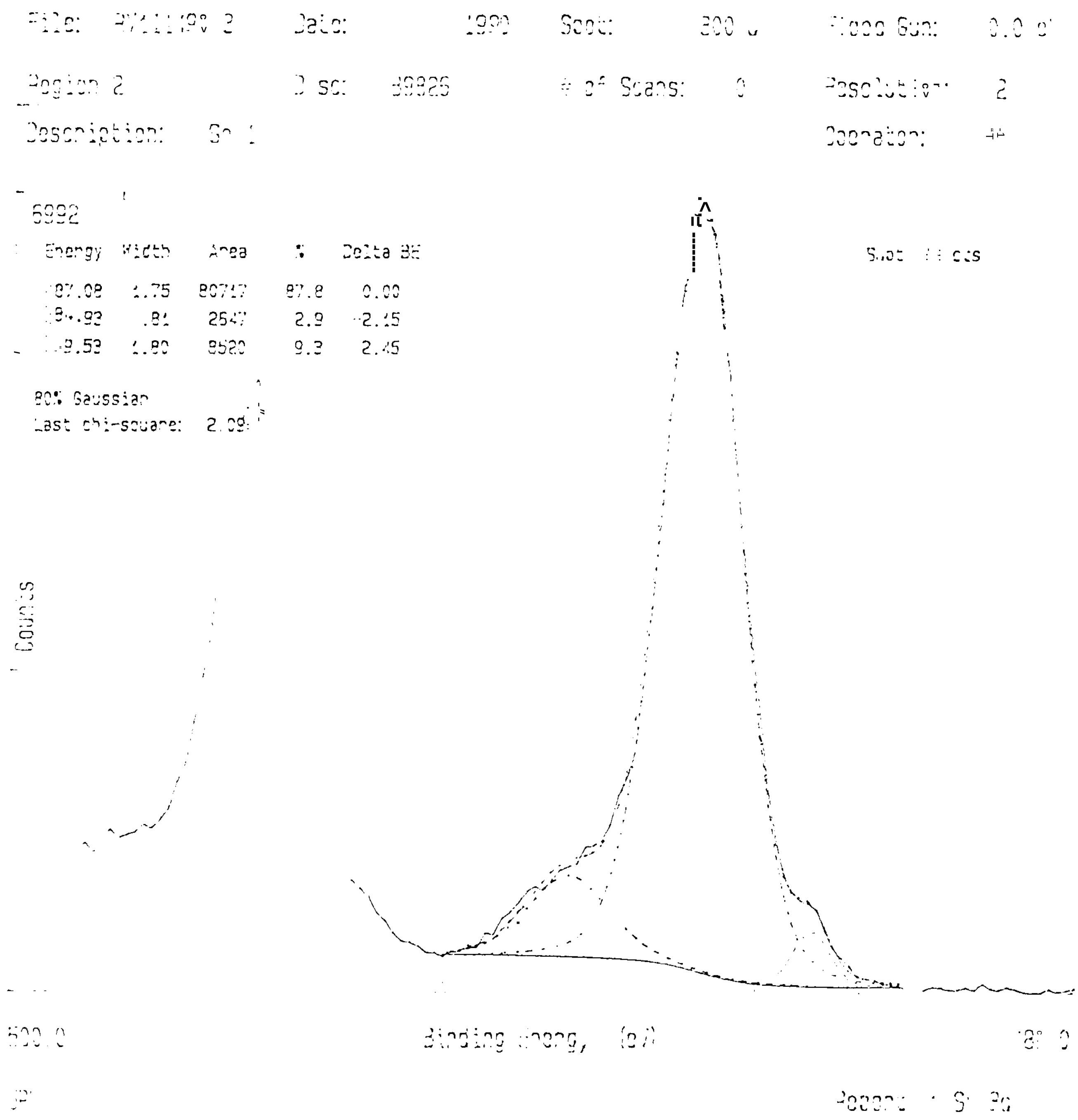

Figure 1Ø.7. XPS Scan of Sn 3d Peaks for Sample Sn-1 Surface

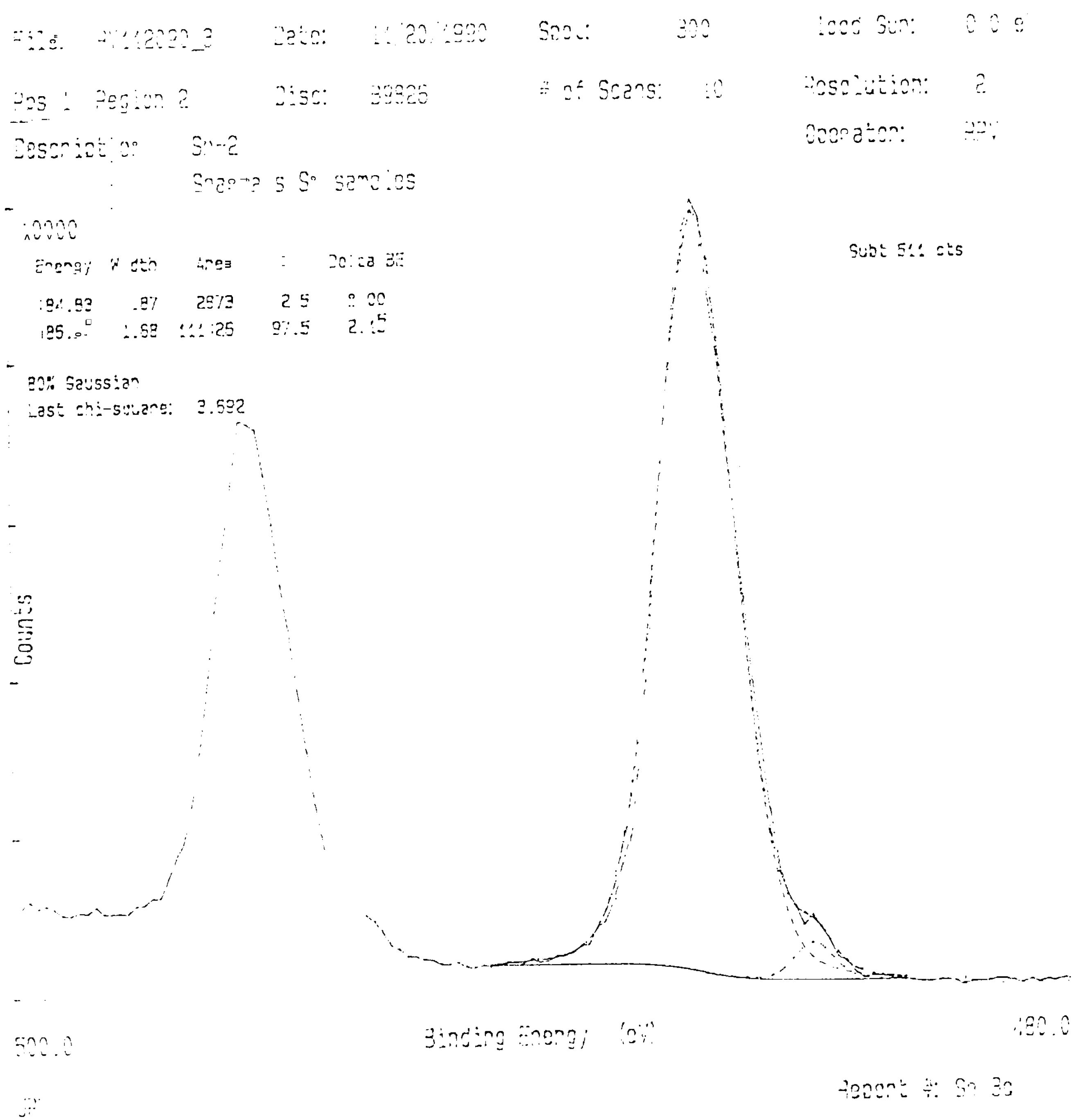

Figure 2.8 XPS Scan of Sn 3d Peaks for Sample Sn-2 Surface

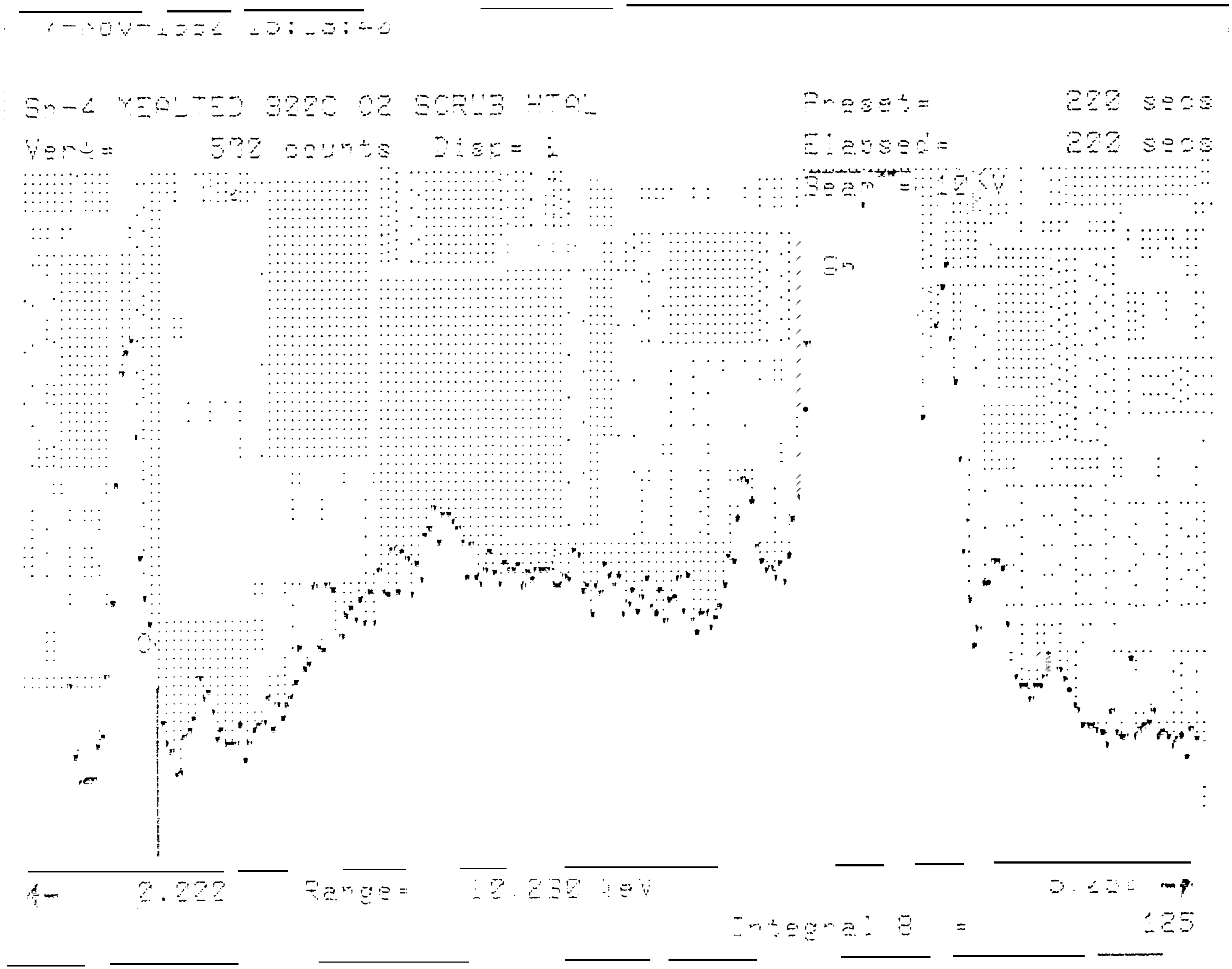

Figure 229 SEM/EDS Scan for Sample Sn-4 Surface

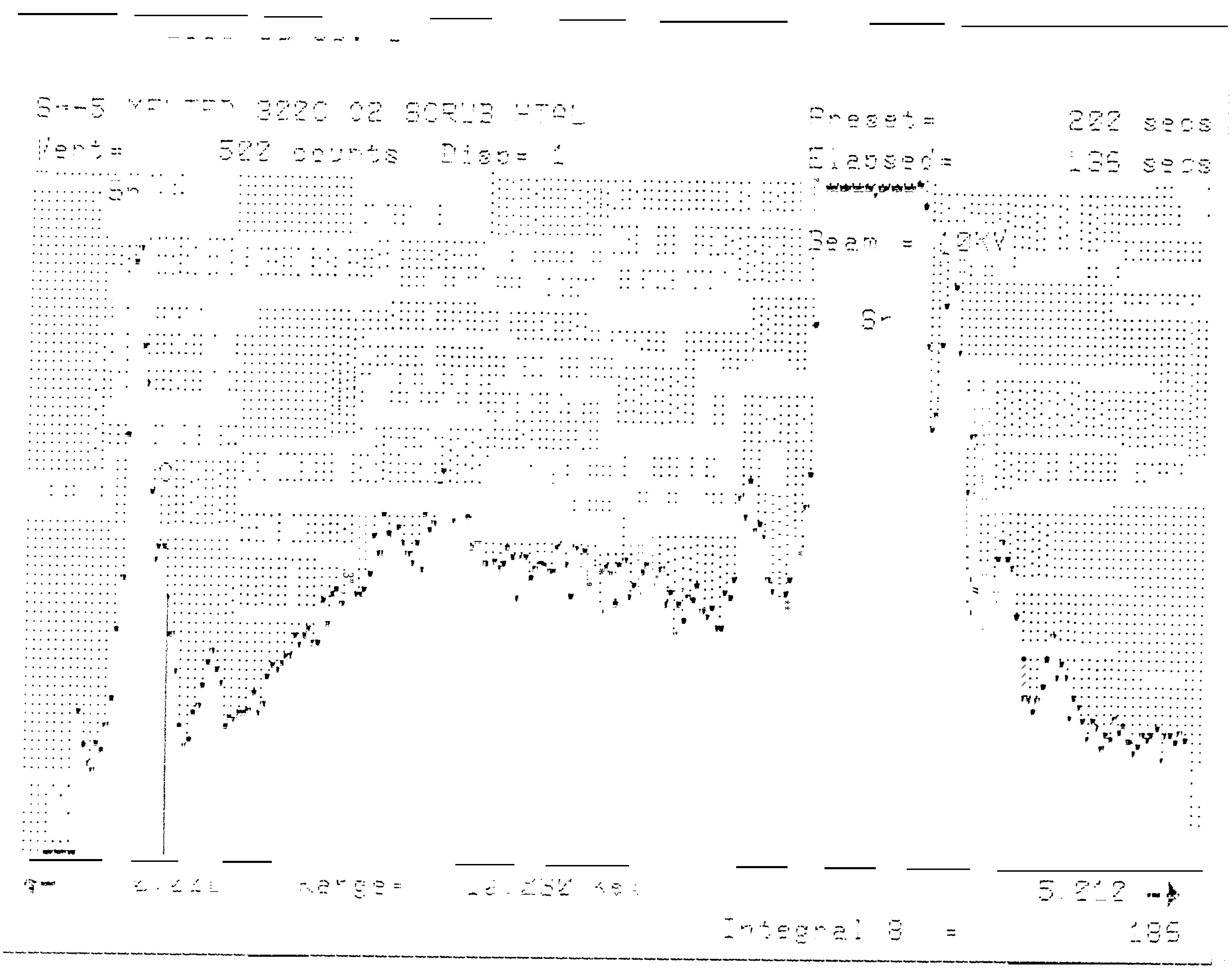

Figure ~~28~~ 10 SEM/EDS Scan for Sample Sn-5 Surface

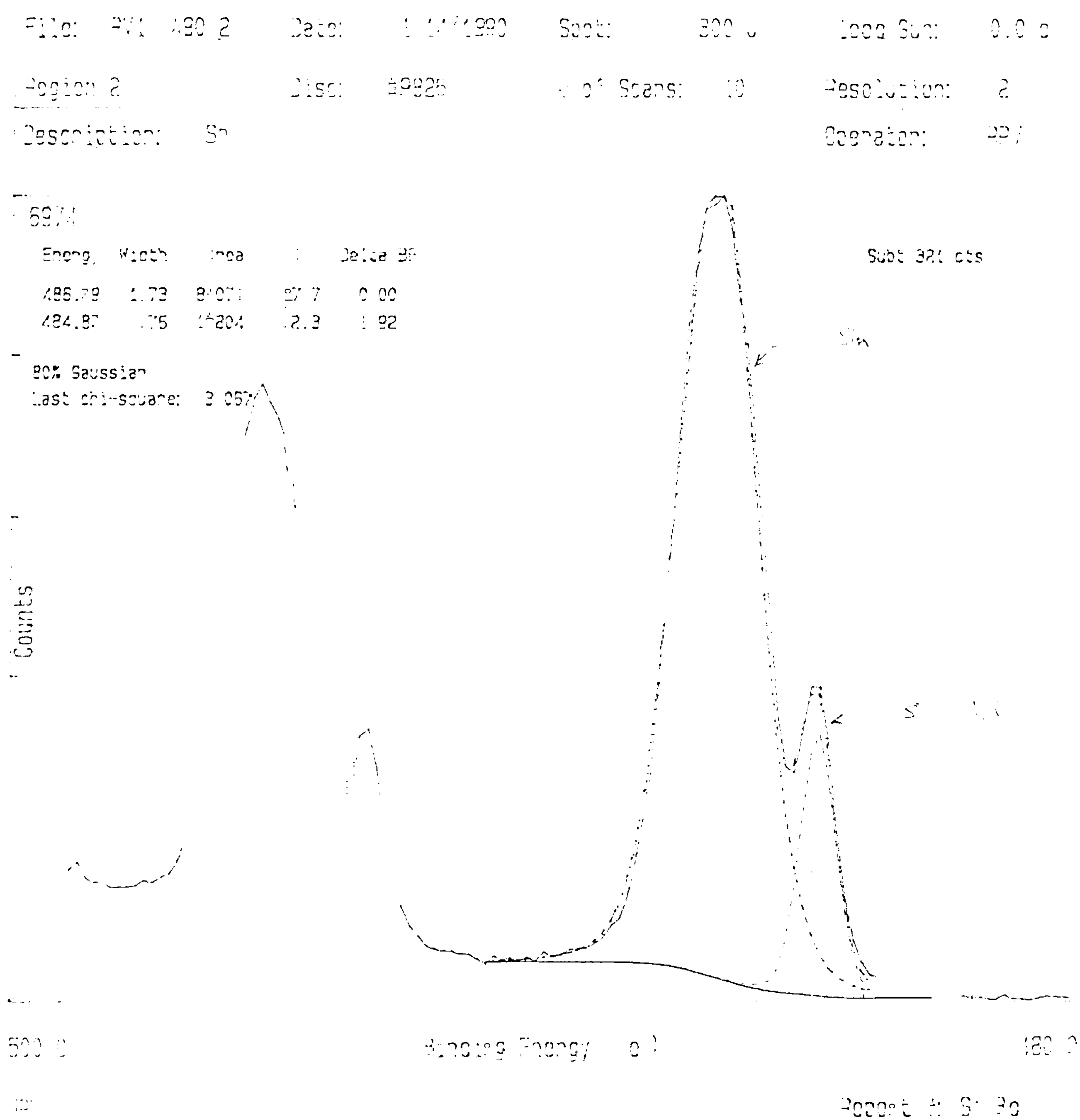

Figure 2511. XPS Scan of Sn 3d Peaks for Sample Sn-4 Surface

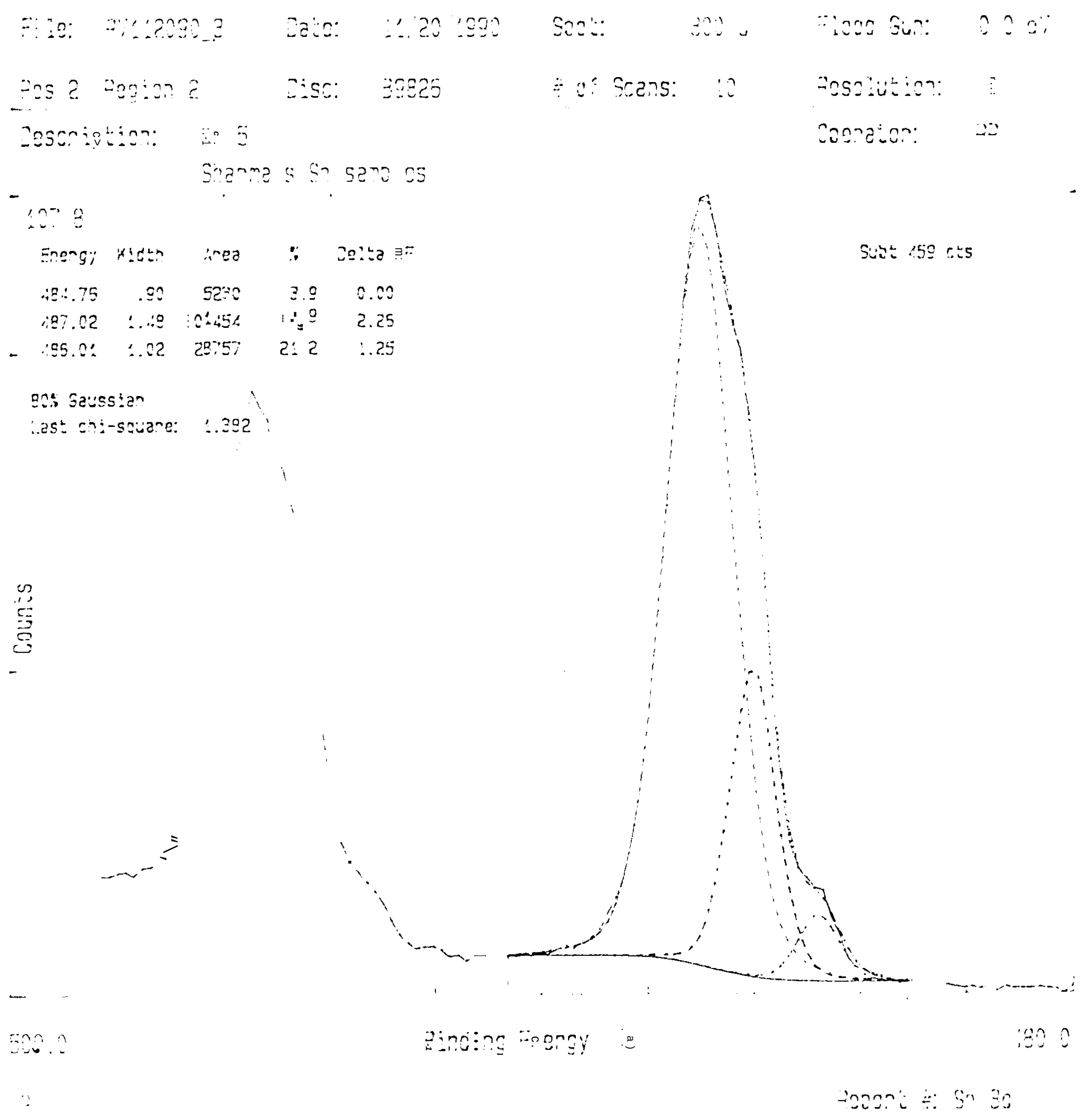

Figure 27/12. XPS Scan of Sn 3d Peaks for Sample Sn-5 Surface

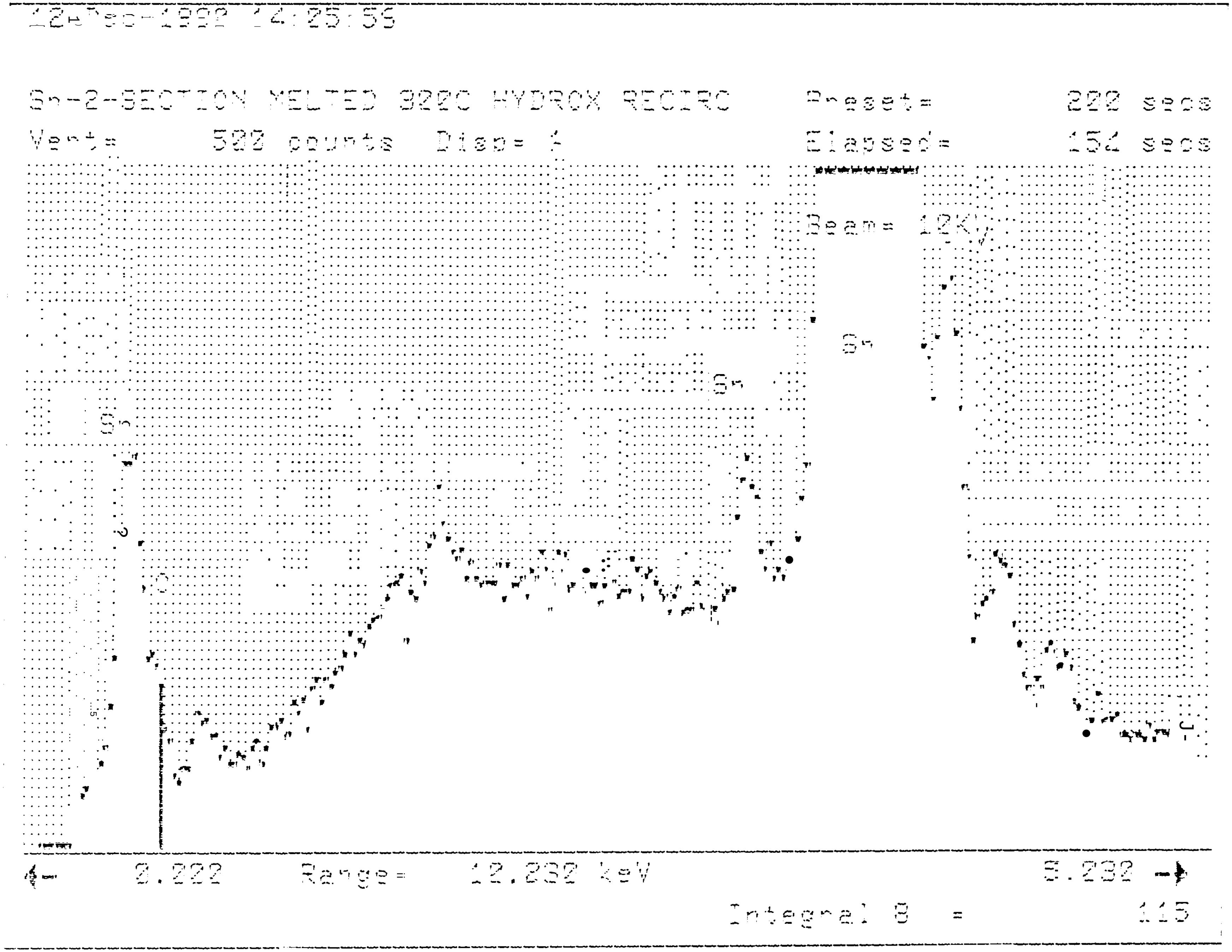

Figure 26/13 SEM/EDS Scan for Sample Sn-2 Cross Section

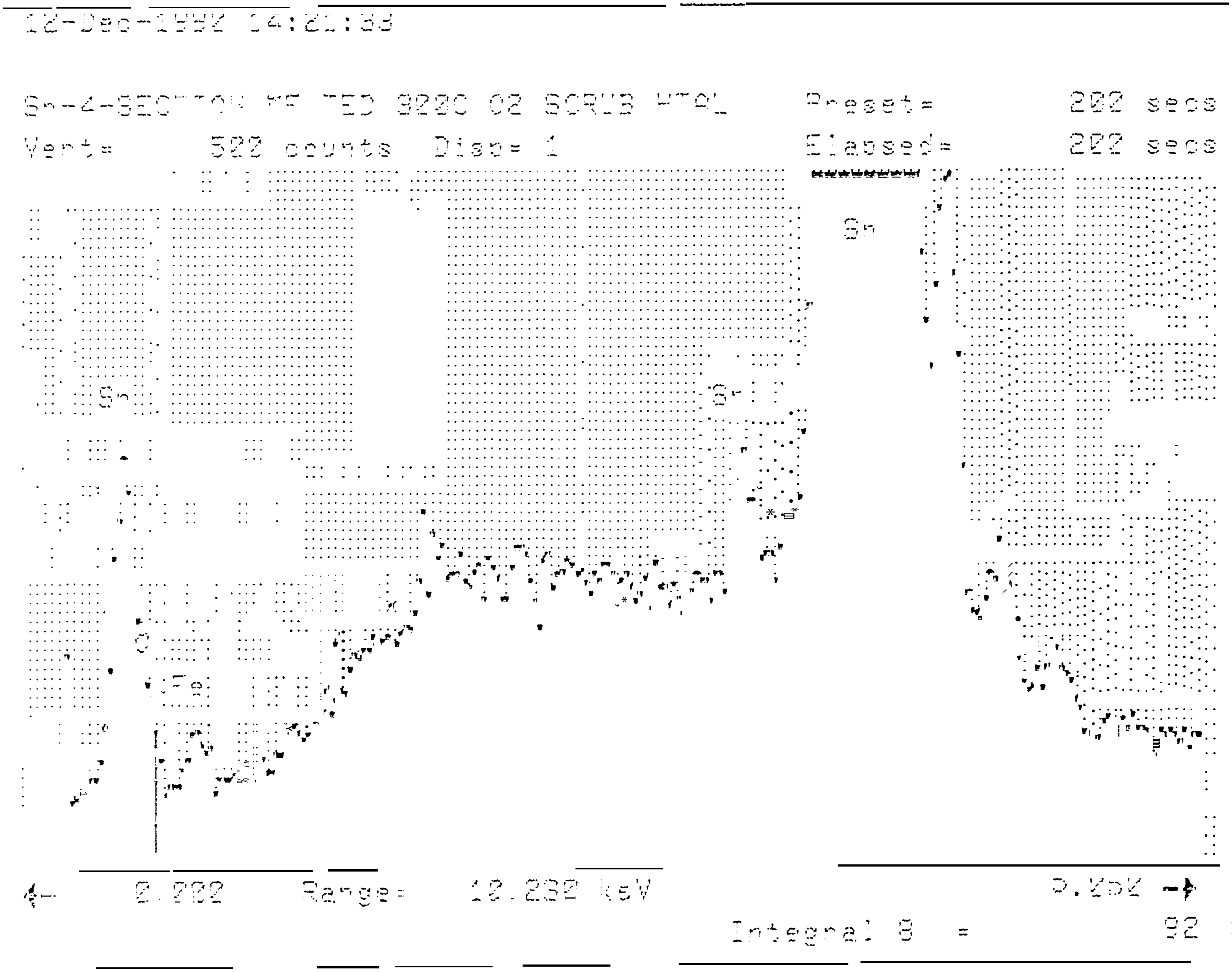

Figure 2014 SEM/EDS Scan for Sample Sn-4 Cross Section

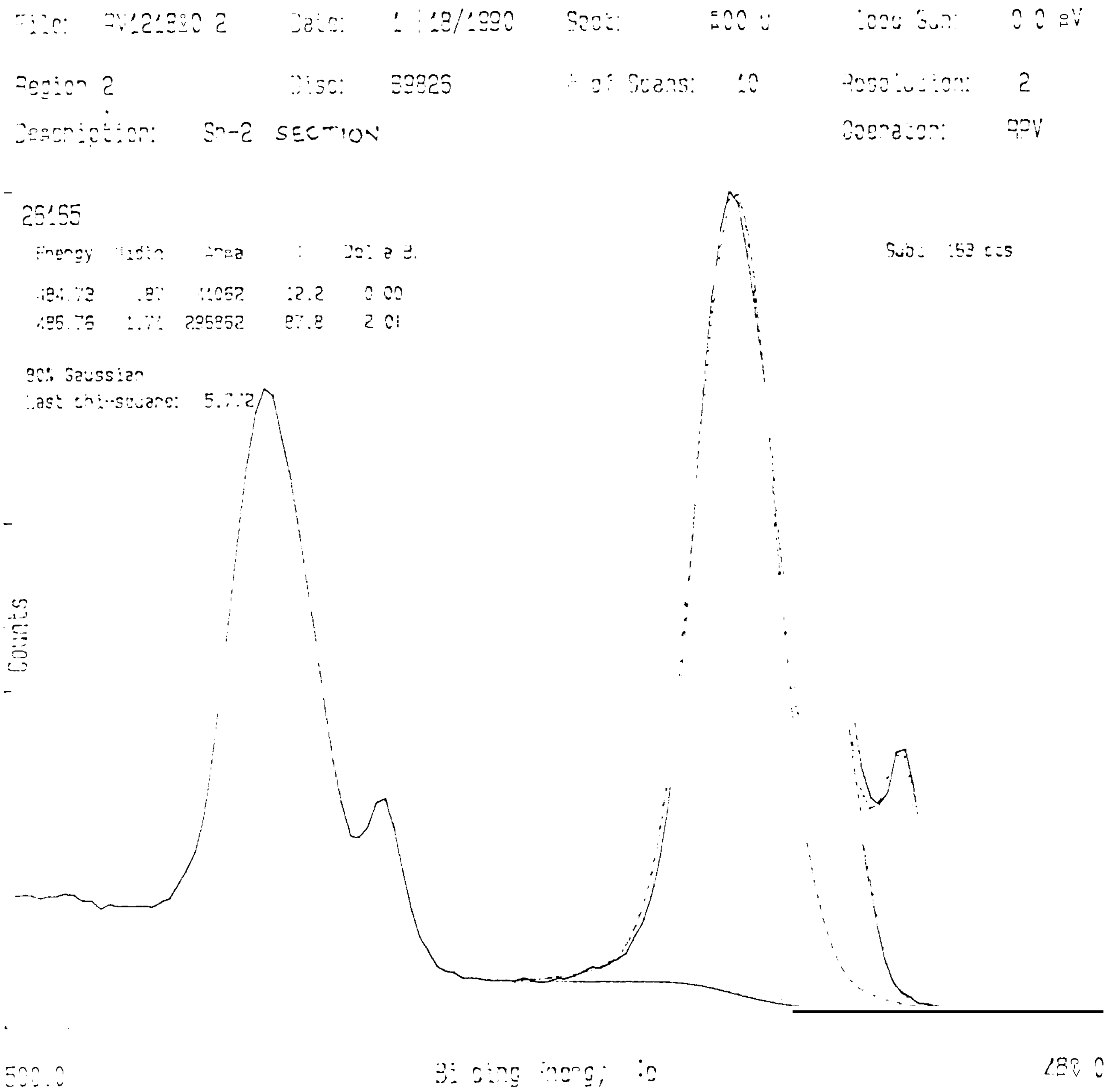

Figure 3/15 XPS for Sn 3d for Sample Sn-2 Cross Section

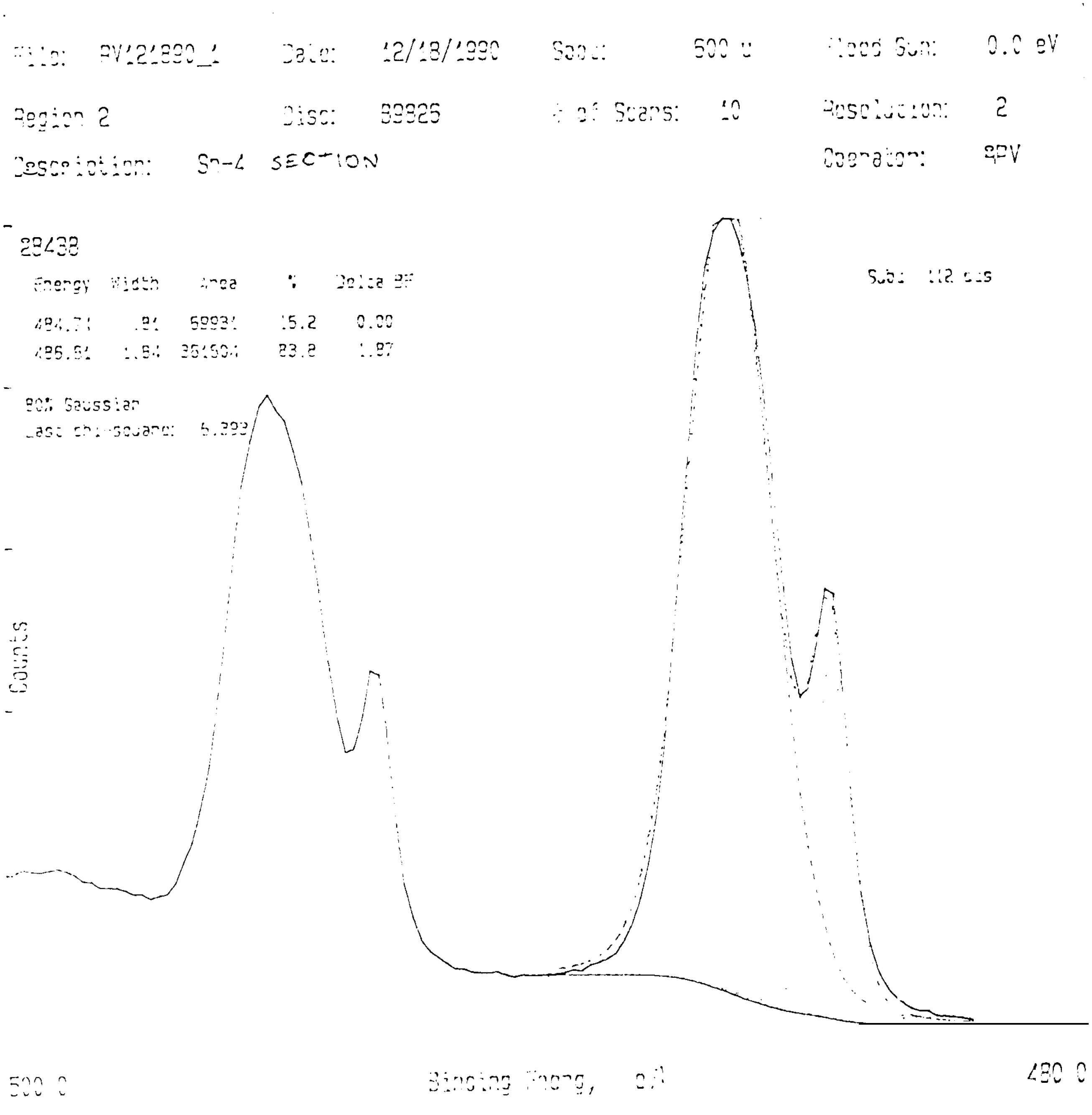

Figure 23 XPS Scan for Sn 3d Peaks for Sample Sn-4 Cross Section